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(19)

(54) FLUORESCENT, MACHINE READABLE INK COMPOSITIONS

(71) We, PITNEY-BOWES, INC., a corporation organised and existing under the laws of the State of Delaware, United States of America, of Walnut and Pacific Sts., Stamford, Connecticut, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:–

In the machine processing of various types of information contained on tickets, tags, labels, postage imprints and the like it is generally known to employ detectors which are responsive to shape relationships and/or colors, and in many cases to the fluorescence of an ink which may be excited, for example, by ultraviolet light. Fluorescent inks and dyes have long been known as, for example, those disclosed in U.S. Patents Nos. 2,681,317; 2,763,785; 3,230,221; 3,412,104; 3,452,075; and 3,560,238. The fluorescent inks and the methods of making or using them as known in the prior art, generally entail the use of a fluorescent ink which, when irradiated, will fluoresce and emit radiation within the wavelength for the particular fluorescent color of that dye or ink. It is known, for example, in the postage meter art to provide a red fluorescent ink for machine reading of processed mail.

The fluorescent detectors, however, are generally designed or set to pick up emissions only within a certain range of wavelengths and accordingly, the coloration of the ink will be dependent upon the formulation which provides for fluorescence under light such as ultraviolet light, to emit radiation of a certain wavelength.

It is desirable, however, to provide tickets, tags, labels, postage meter imprints, stampings, or the like with a greater variety of visual color for classification, for inventory purposes or sorting, for example, so that the tags, tickets, envelopes and the like are, or may be, processed visually by people, as well as by one or more machines. A problem arises, however, when a variety of visual colors are used since the visual color is generally related to the fluorescent.

The present invention provides a novel ink composition wherein the fluorescent colour of ink under irradiation is different from that of the ink under mixed light conditions, so that the visual colours of the inks may be used for visual sorting as well as the fluorescent colour for machine sorting.

In accordance with the invention, there is provided a fluorescent marking ink having a first colour when viewed under mixed light conditions and a second colour, different from the first, when viewed under conditions causing fluorescence of the said fluorescent ink, said ink comprising a liquid vehicle and dispersed therein a) from 0.3 to 10% by weight, based on the total ink composition, of a non-fluorescent pigment and b) from 2 to 25% by weight, based on the total composition, of a fluorescent pigment, having a fluorescent colour different from that of the colour, under mixed light, of the non-fluorescent pigment, said fluorescent pigment being selected from

a) dispersions of a fluorescent pigment in a solution of a resin dissolved in a narrow fraction petroleum distillate boiling in the range 440 – 510°F;
b) dispersions of a fluorescent pigment in a drying-type alkyl resin; and
c) a comminuted solid solution of a fluorescent dye in a modified sulfonamide resin, wherein said liquid vehicle comprises a mixture of a) dioctyl phthalate and b) an aliphatic hydrocarbon distilling in the range 310 – 345°C.

Also provided is a method of processing an article, which comprises marking that article

with an ink as defined above, passing that article, when so marked, through a machine equipped with a sensor sensitive to the fluorescent wavelength of said fluorescent pigment and with a means, responsive to said sensor, for performing an operation on that article, and exposing that article whilst in the machine with radiation capable of exciting the fluorescent pigment and causing the same to fluoresce.

The pigment combination which is characteristic of the ink compositions of this invention may provide a variety of colours to the eye or to an optical reader, but all provide for fluorescent emission, preferably within a relatively narrow wavelength, to make it possible to machine read tickets, labels, mail or the like with a single setting of a fluorescent detector device while providing for a variety of visually differing colours. The visually different colours can be also optically read by a machine to provide a second mark or set of data from that read by the fluorescent detector. The visual colour of the ink is preferably a colour other than red or orange while the fluorescent colour of the ink is preferably red or orange.

In accordance with this invention, machine readable tickets, tags, labels, postage imprints and the like may be provided with a visual colour, i.e. a colour under ordinary mixed light frequencies and a fluorescent radiation colour which when irradiated with ultra-violet light, for example, fluoresces preferably in the red wavelength of from 5800°A to 6200°A. Since there are existing machines for reading fluorescent ink imprinted information, a variety of visual colours can be employed with the fluorescent colour of the ink being within the red portion of the spectrum. Thus the ink imprint may be read visually or by some other type of optical machine reader and then read by a fluorescent machine reader which is set to pick up the fluorescent wavelength of the ink. This is particularly useful in the field of postage imprinting since at large postal installations machines may be available to read postage information, but at many smaller or rural stations the postage imprint must be visually read. Further, by the use of a visual or optical color which is different from the fluorescent color a combination of information may be imprinted which is readable by two different machines, i.e. an optical reader which is responsive to the reflected color and/or shape of the imprint under ordinary mixed light and a fluorescent reader which responds to the particular fluorescent wavelength when the ink is irradiated.

The inks may have ordinary mixed light colors of orange, brown, purple, black, blue or green, for example, while emitting orange-red fluorescence when activated by long or short ultraviolet waves. The general formulation is a combination of fluorescent and optical pigments with the fluorescent pigment constituting from 2 to 25%, preferably from 10 to 20%, by weight, and the non-fluorescent pigment constituting from 0.3 to 10%, preferably from 0.5 to 2.5% by weight, of the total composition. The pigments are carried in a liquid vehicle comprising a mixture of dioctyl phthalate (DOP) and an aliphatic hydrocarbon having a distillation range 310° to 345°C., e.g. that sold by East Coast Chemicals Co. as "Escoflex 175." The ratio of dioctyl phthalate to the aliphatic hydrocarbon is preferably about 3:1 by weight. To the vehicle there may be added from .25 to 1.5% surfactant and from .25 to 5% gellant all by weight. The preferred surfactant is lecithin and the preferred gellant is aluminum stearate having a high free stearic acid content made up as a 10% gel in a vehicle which is the same or is compatible with the ink vehicle. There may also be added up to 1% antioxidant and the preferred antioxidant is eugenol.

The fluorescent pigments used in this invention are i) dispersions of a fluorescent pigment in a heat-set type vehicle which is either a resin dissolved in a high boiling (440–510°F) narrow fraction petroleum distillator a drying type alkyd resin, such as Trionol No. 3 (Registered Trade Mark) sold by Lawter Chemicals, Inc., or ii) a comminuted solid solution of a fluorescent dye in a modified sulfonamide resin, for example a thermo-plastic melamine-sulfonamide-formaldehyde resin. The other pigments used as set forth in the Examples below are used to impart the desired visual colour which is different from the fluorescent colour under ultraviolet light. The non fluorescent pigments are generally in a heat-set type vehicle, e.g. a litho varnish, or preferably a mixture of dioctyl phthalate and an aliphatic hydrocarbon having a distillation range of 310°C to 345°C, preferably in a weight ratio of about 3:1. This is set forth as PRV (porous roller vehicle) in the Examples below.

The following Examples are exemplary of the invention and should not be considered limiting. In the Examples, the fluorescent pigments are those designated D516, H6118, H622, H618 and H636 and the non-fluorescent pigments are those designated FS 1117, FL–10–707, W–92, 5–65–F–423, FL–15–403 and FS1116.

EXAMPLE I

Orange	% By Weight in Ink	Commercial Designation	% By Weight in Ink (incl. vehicle	Source
Strong Red Orange	7.70	D516 Dispersion	15.40	Lawter Chemicals, Inc.
Benzidine Yellow	1.50	FS1117 Thermex Flush	6.00	Chemetron Corp.
Brilliant Toning Red	0.80	FL–10–707 PRV Flush	1.77	Sherwin Williams Chemicals
Aluminum Stearate 132	0.50	10% Gel In PRV	5.00	Witco Chemical Corp.
Polyvinyl Chloride	0.12	Marvinol 50 3% Gel In PRV	4.00	Uniroyal, Inc.
Lecithin U.H.	0.50	Lecithin U.F.	0.50	A.E. Staley Mfg. Co.
Eugenol	0.50	Eugenol U.S.P.	0.50	Fritzsche Dodge & Alcott, Inc.
Vehicles	88.38	DOP PX–138	50.13	U.S.Steel Corp., Chemical Div.
		Escoflex 175	16.71	East Coast Chemicals Co.

The procedure used for a 100 pound batch of ink in accordance with this Example is as follows. First the dioctyl phthalate (DOP), Escoflex 175, eugenol and lecithin are weighed into a ten gallon tank and mixed to form the vehicle solution. The gel(s) and pigments are then weighed into a twenty gallon mixing vessel and blended with a mixer such as a Cowles mixer until the mixture is uniform which should take about 15 to 20 minutes. If there are any undispersed gels or pigments the stirring should continue until the mixture is uniform. The gel pigment dispersion is continued to be stirred and 1–½ to 2 gallons of the vehicle solution is added to the dispersion and is stirred for a period of about 5 to 10 minutes before the addition of the remaining vehicle solution. The ink is then stirred for about 30 minutes more and is then strained through four to six layers of cheesecloth before it is run on an Eppenbach high-speed mixer for about 15 minutes. The ink is then allowed to stand for 10 hours or more (such as over night) and is then stirred for about 15 minutes with a propeller mixer and again for 15 additional minutes with a high-speed mixer, again allowed to stand for over 10 hours and is then stirred once more with a propeller mixer, after which it is ready for use.

EXAMPLE II

The procedure for preparing the ink in this Example is the same as that set forth in Example I, above, except that the formulation is as follows:

Brown	% By-Weight	Commercial Designation	% by Weight in Ink (incl. vehicle)	Source
High Intensity Yellow Orange	13.98	H6118 Dispersion	27.96	Lawter Chem.
Carbon Black	0.87	W–92 Flush	3.06	Chemetron Corp.
Phthalocyanine Green	0.15	5–65–F–423 Flush	0.43	Hilton Davis Div. Sterling Drug, Inc.
Aluminum Stearate 132	0.50	10% Gel in PRV	5.00	
Lecithin U.F.	0.50	Lecithin U.F.	0.50	
Eugenol	0.25	Eugenol U.S.P.	0.25	
Vehicles	83.75	DOP PX–138	47.10	
		Escoflex 175	15.70	

EXAMPLE III

The procedure for preparing the ink in this Example is the same as that set forth in Example I, above, except that the formulation is as follows:

Purple	% By Weight	Commercial Designation	% by Weight in Ink (incl. vehicle)	Source
Pink	1852	H622 Dispersion	37.04	Lawter Chemicals
Alkali Blue G.G.	0.37	FL–15–403 Flush	1.09	Sherwin Williams
Aluminum Stearate	0.50	10% Gel in PRV	5.00	
Lecithin U.S.	0.50	Lecithin U.F.	0.50	
Eugenol U.S.P.	0.25	Eugenol U.S.P.	0.25	
Vehicles	79.86	DOP PX–138	42.09	
		Escoflex 175	14.03	

EXAMPLE IV

The procedure for preparing the ink in this Example is the same as that set forth in Example I, above, except that the formulation is as follows:

Black	% By Weight	Commercial Designation	% By Weight in Ink (incl. Vehicle)	Source
Strong Yellow Orange	17.09	H618 Dispersion	34.18	
Alkali Blue G.G.	0.73	FL–15–403	2.15	
Aluminum Stearate 132	0.50	10% Gel in PRV	5.00	
Lecithin U.F.	0.50	Lecithin U.F.	0.50	
Eugenol U.S.P.	0.25	Eugenol U.S.P.	0.25	
Vehicles	80.93	DOP PX–138	43.44	
		Excoflex 175	14.48	

EXAMPLE V

The procedure for preparing the ink in this Example is the same as that set forth in Example I, above, except that the formulation is as follows:

Blue	% By Weight	Commercial Designation	% by Weight in Ink (incl. Vehicle)	Source
Strong Red	9.00	H636 Dispersion	18.00	Lawter Chemicals
Phthalocyanine Blue	1.00	FS1116 Flush	3.57	Chemetron
Aluminum Stearate	0.50	10% Gel in PRV	5.00	
Lecithin U.F.	0.50	Lecithin U.F.	0.50	
Eugenol	0.25	Eugenol U.S.P.	0.25	
Vehicles	88.75	DOP PX–138	54.51	
		Escoflex	18.17	

EXAMPLE VI

The procedure for preparing the ink in this Example is the same as that set forth in Example I, above, except that the formulation is as follows:

Green	% By Weight	Commercial Designation	% By Weight in Ink (incl. Vehicle)	Source
Strong Yellow Orange	10.55	H618 Dispersion	21.10	
Phthalocyanine Green	1.58	5–65–F–423 Flush	4.51	
Strong Lemon Yellow	3.16	D541 Dispersion	6.32	Lawter Chemicals
Aluminum Stearate	0.50	10% Gel in PRV	5.00	
Lecithin U.F.	0.50	Lecithin U.F.	0.50	
Eugenol	0.25	Eugenol U.S.P.	0.25	
Vehicles	83.46	DOP PX–138	46.74	
		Excoflex 175	15.58	

In the above Examples the same constituents contain a fraction of solids by weight which accounts for the differences in the percentages of the constituent alone versus the constituent-plus vehicle which is admixed to make the ink composition.

In the above Examples the aluminum stearate 132 has a high free stearic acid content and the polyvinyl chloride used had an inherent viscosity of 1.20 and a specific viscosity of 0.50. The carbon black in the above Examples may be any suitable pigment black, and for the above Examples the carbon black was dispersed in a gloss-type vehicle. The non-fluorescent pigments are known such as benzidine yellow which is a common yellow pigment which is flushed in a heat-set type vehicle. The brilliant toning red pigment is also identified as Permanent Red 2B (Color Index 15865 – Pigment Red 48) which is flushed in porous roller vehicle. The phthalocyanine Green is Pigment Green 7 (Color Index 74260) which is flushed in a litho varnish. It is designated by the supplier (Hilton Davis) as Synthaline Green. The Alkali Blue GG is a well known Pigment Blue 19 (Color Index 42750A) which is also flushed in a litho varnish. The Phthalocyanine Blue is Pigment Blue 15 (Color Index 74160) which is flushed in a heat-set type vehicle.

The ink can be applied in a number of ways by stamps, from rollers or by an appropriate printing device. While fluorescent wavelengths of other than red or red-orange may be employed, a red or red-orange is preferred since there are existing detectors which are specifically designed for this wavelength of fluorescent radiation. In any event the fluorescent emission should be within certain limits of wavelength so that there is no need to continually adjust or reset the fluorescent detector each time a new color is being processed. Thus in accordance with the invention a number of visual colors may be imprinted, but will all be machine readable by at least the same fluorescent detector.

In practice, for example, when used for postage imprinting the ink may be carried on or in rollers, belts, pads, or the like for transferring the proper print configuration to a letter or postage imprint tape. Once imprinted the mail-carrying imprint with such ink can be checked visually by the human eye or, depending upon the postage imprint configuration, by an optical detector which may be activated by the reflection of ordinary mixed light from the postage imprint. The same or other portions of the postage imprint may be further read by a fluorescent detector when the postage imprint is subjected to, for example, ultraviolet radiation. Additional information contained in the postage imprint can be picked up by the fluorescent detector. Mail sorting and routing, as well as the machine verification of postage amounts and other such functions, can be facilitated by the dual emissive ink in accordance with the invention. Similarly, the method of the invention may be employed in the marking of retail price tickets and the like to provide dual emissive characteristics for machine sorting and/or compilation of sales or inventory information.

The ink may also be used to verify the source of products. Phonograph records, for example, may be marked with the dual emissive ink and by detection of the fluorescent color by machine, counterfeit records may be separated from the genuine ones.

WHAT WE CLAIM IS:-

1. A fluorescent marking ink having a first colour when viewed under white light conditions and a second colour, different from the first, when viewed under black light conditions causing fluorescence of the said fluorescent ink, said ink comprising a liquid vehicle and dispersed therein a) from 0.3 to 10% by weight, based on the total ink composition, of a non-fluorescent pigment and b) from 2 to 25% by weight, based on the total composition, of a fluorescent pigment, having a fluorescent colour different from that of the colour, under mixed light, of the non-fluorescent pigment, said fluorescent pigment being selected from
   a) dispersions of a fluorescent pigment in a solution of a resin dissolved in a narrow fraction petroleum distillate boiling in the range 440 – 510°F;
   b) dispersions of a fluorescent pigment in a drying-type alkyd resin and
   c) a comminuted solid solution of a fluorescent dye in a modified sulfonamide resin, wherein said liquid vehicle comprises a mixture of a) dioctyl phthalate and b) an aliphatic hydrocarbon distilling in the range 310 – 345°C.

2. An ink according to claim 1 wherein components a) and b) of the liquid vehicle are present in a weight ratio of 3:1.

3. An ink according to claim 1 or 2, wherein the fluorescent pigment fluoresces at a wavelength of from 5800 to 6200 Angstroms.

4. An ink according to any one of claims 1–3, containing from 0.25 to 1.5% by weight, based on the total composition, of a surfactant.

5. An ink according to claim 4, wherein the surfactant is lecithin.

6. An ink according to any one of claims 1–5, containing from 0.25 to 5% by weight, based on the total composition of a gellant.

7. An ink according to claim 6, wherein the gellant is aluminium stearate.

8. An ink according to any one of the preceding claims, wherein the fluorescent colour of the ink is red or orange, and the colour of the ink under mixed light is other than orange or red.

9. An ink according to claim 1, substantially as hereinbefore described in any one of the foregoing Examples.

10. A method of processing an article, which comprises marking that article with an ink as claimed in any one of the preceding claims, passing that article, when so marked, through a machine equipped with a sensor sensitive to the fluorescent wavelength of said fluorescent pigment and with a means, responsive to said sensor, for performing an operation on that article, and exposing that article whilst in the machine with radiation capable of exciting the fluorescent pigment and causing the same to fluoresce.

11. A method according to claim 10, wherein the marked article is also optically processed under mixed light conditions and a second operation performed on that article in response to the mixed light colour of said mark.

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